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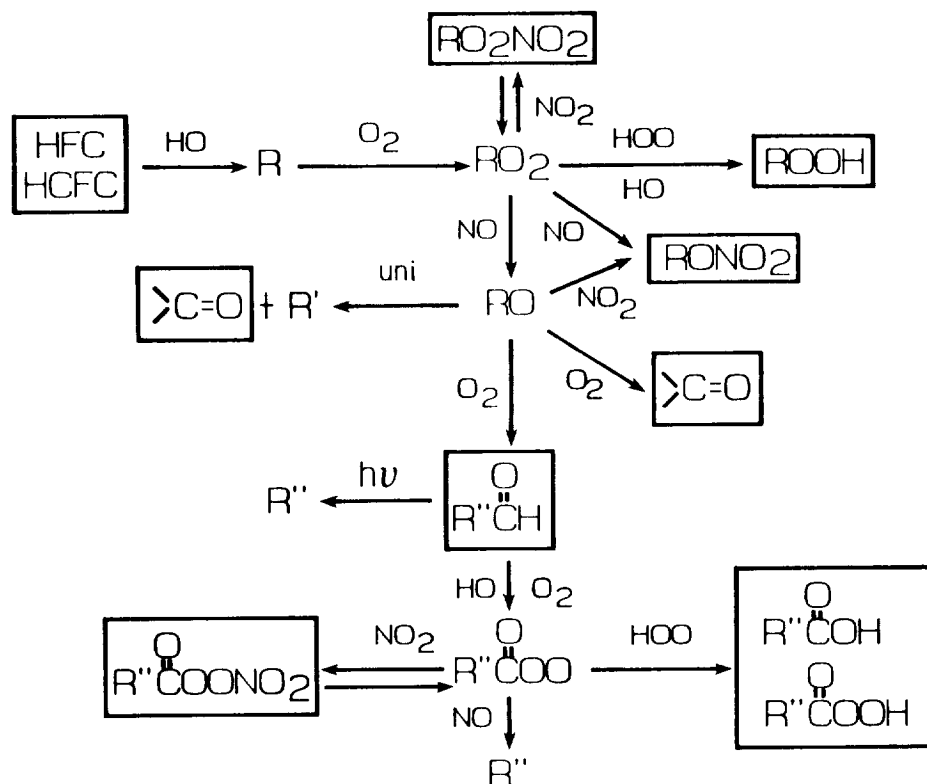
**AN ASSESSMENT OF POTENTIAL DEGRADATION PRODUCTS IN THE GAS-PHASE
REACTIONS OF ALTERNATIVE FLUOROCARBONS IN THE TROPOSPHERE**

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EXECUTIVE SUMMARY

Tropospheric chemical transformations of alternative hydrofluorocarbons (HCFs) and hydrochlorofluorocarbons (HCFCs) are governed by hydroxyl radical initiated oxidation processes, which are likely to be analogous to those known for alkanes and chloroalkanes. A schematic diagram, shown below, illustrates plausible reaction mechanisms for their atmospheric degradation; where R, R' and R'' denote the F- and/or Cl-substituted alkyl groups derived from HCFs and HCFCs subsequent to the initial H atom abstraction by HO radicals. At present, virtually no kinetic data exist for the majority of these reactions, particularly for those involving RO. Potential degradation intermediates and final products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates, as summarized in the attached table. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products shown in this table, there seem to be no significant gas-phase removal mechanisms. Further chemical kinetics and photochemical data are needed to quantitatively assess the atmospheric fate of HCFs and HCFCs, and of the degradation products postulated in this report.



Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

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Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	HCCl ₂ CF ₃	CF ₃ CCl ₂ OO CF ₃ CCl ₂ O CF ₃ OO CF ₃ O	CF ₃ CClO		CF ₃ CCl ₂ OOH CF ₃ OOH CF ₃ OH	CF ₃ CCl ₂ OONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂
HCFC 141B	CCl ₂ FCH ₃	CCl ₂ FCH ₂ OO CCl ₂ FCH ₂ O CCl ₂ FOO CCl ₂ FO CCl ₂ FC(O)OO	CCl ₂ FCHO CClFO	CCl ₂ FC(O)OOH CCl ₂ FC(O)OH	CCl ₂ FCH ₂ OOH CCl ₂ FOOH	CCl ₂ FCH ₂ OONO ₂ CCl ₂ FOONO ₂ CCl ₂ FC(O)OONO ₂
HCFC 142b	CClF ₂ CH ₃	CClF ₂ CH ₂ OO CClF ₂ CH ₂ O CClF ₂ OO CClF ₂ O CClF ₂ C(O)OO	CClF ₂ CHO CF ₂ O	CClF ₂ (O)OOH CClF ₂ C(O)OH	CClF ₂ CH ₂ OOH CClF ₂ OOH	CClF ₂ CH ₂ OONO ₂ CClF ₂ OONO ₂ CClF ₂ C(O)OONO ₂
HCFC 22	CHClF ₂	CClF ₂ OO CClF ₂ O	CF ₂ O		CClF ₂ OOH	CClF ₂ OONO ₂
HCFC 124	CHClFCH ₃	CF ₃ CClFOO CF ₃ CClFO CF ₃ OO CF ₃ O	CF ₃ CFO		CF ₃ CClFOOH CF ₃ OOH CF ₃ OH	CF ₃ CClFOONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂
HCF 134a	CH ₂ FCF ₃	CF ₃ CHFOO CF ₃ CHFO CF ₃ OO CF ₃ O CFO	CHFO CF ₃ CHFO		CF ₃ CHFOOH	CF ₃ CHFOONO ₂
HFC 52a	CHF ₂ CH ₃	CH ₃ CF ₂ Oo CH ₃ CF ₂ O CHF ₂ CH ₂ OO CHF ₂ CH ₂ O CHF ₂ OO CHF ₂ O CHF ₂ C(O)OO CFO	CF ₂ O CHF ₂ CHO CHFO	CHF ₂ C(O)OOH CHF ₂ C(O)OH CF(O)OOH	CH ₃ CF ₂ OOH CHF ₂ CH ₂ OOH CHF ₂ OOH	CH ₃ CF ₂ OONO ₂ CHF ₂ CH ₂ OONO ₂ CHF ₂ OONO ₂ CHF ₂ C(O)OONO ₂ CF(O)OONO ₂
HCF 125	CHF ₂ CF ₃	CF ₃ CF ₂ OO CF ₃ CF ₂ O CF ₃ OO CF ₃ O	CF ₂ O CF ₃ CFO		CF ₃ CF ₂ OOH CF ₃ OOH CF ₃ OH	CF ₃ CF ₂ OONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂

1. INTRODUCTION

As part of the AFEAS (Alternative Fluorocarbon Environmental Acceptability Study) program for evaluating all relevant current scientific information to determine the environmental acceptability of the alternative fluorocarbons, the following list of questions concerning their atmospheric degradation via gas-phase chemical reactions will be addressed in this report.

1. How will alternative fluorocarbons degraded in the troposphere after initial hydrogen abstraction by hydroxyl (HO) radicals?
2. What are the intermediate and final products of the gas-phase chemical reactions?
3. What are the most probable gas-phase chemical lifetimes of these products in the troposphere?
4. Is it likely that relatively stable fluorine containing products would be formed?
5. How would the degradation products be removed from the atmosphere via gas-phase chemical reactions?

Alternative fluorocarbons under consideration include all HFCs and HCFCs given, respectively, by the formula $\text{CH}_{4-n}\text{F}_n$ ($1 \leq n \leq 3$), $\text{C}_2\text{H}_{6-n}\text{F}_n$ ($1 \leq n \leq 5$), and $\text{CH}_{4-m-n}\text{Cl}_m\text{F}_n$ ($1 \leq m \leq 2$; $1 \leq n \leq 2$; $m + n \leq 3$) and $\text{C}_2\text{H}_{6-m-n}\text{Cl}_m\text{F}_n$ ($1 \leq m \leq 4$; $1 \leq n \leq 4$; $m + n \leq 5$), but emphasis will be placed on HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The formulas for these fluorocarbons are listed in table 1 along with the expected initial radicals following reaction with HO radicals.

Questions 1 and 2 deal with the formation of fluorine or chlorine-containing molecular products via the gas-phase HO-initiated reactions of HFCs and HCFCs under representative tropospheric conditions, and questions 3-5 with the subsequent removal of these products by either direct photodissociation or reactions with gaseous tropospheric constituents. These topics are discussed in Sections I and II, respectively. Products with sufficiently long lifetimes are eventually removed from the troposphere by processes such as rain out, deposition to the earth's surface or escape into the stratosphere. These heterogeneous removal processes are evaluated elsewhere in the AFEAS program and will not be discussed in this report.

The HO-radical initiated degradation of HFCs and HCFCs in the troposphere takes place via a large number of reactions involving free radical intermediates. A literature review is given in the appendix. Many of these reaction steps have not been determined experimentally. Thus, when judged plausible, available information on analogous reactions and thermochemical data are also utilized (stated as such) in this evaluation.

2. ATMOSPHERIC DEGRADATION MECHANISMS

Listed in Table 1 are all the possible fluorine- and/or chlorine-substituted haloalkyl (R) radicals initially formed from HFCs and HCFCs after H atom abstraction by HO radicals. As discussed later in the Appendix, atmospheric degradation mechanisms of these R radicals appear to be, in large part, analogous to those of the corresponding alkyl radicals, i.e. CH_3 and C_2H_5 (NASA Report, 1987; CODATA, 1982; Kerr and Calvert, 1984; Atkinson, 1986). These reaction steps involve various types of free radicals and molecular products and are illustrated schematically in Figure 1. In this figure, the molecular products

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Table 1: List of Alternative Fluorocarbons and Primary Radicals

Compound	m	n	Formula	Primary Radical
HFC				
$\text{CH}_{4-n}\text{F}_n$ ($1 \leq n \leq 3$)		1	CH_3F	CH_2F
		2	CH_2F_2	CHF_2
		3	CHF_3	CF_3
$\text{C}_2\text{H}_{6-n}\text{F}_n$		1	$\text{CH}_3\text{CH}_2\text{F}$	$\text{CH}_3\text{CHF}; \text{CH}_2\text{FCH}_2$
		2	CH_3CHF_2 (152a)	$\text{CH}_3\text{CF}_2; \text{CHF}_2\text{CH}_2$
			$\text{CH}_2\text{FCH}_2\text{F}$	CH_2HCHF
		3	CH_3CF_3	CF_3CH_2
			CH_2FCHF_2	$\text{CH}_2\text{FCF}_2; \text{CHF}_2\text{CHF}$
		4	CH_2FCF_3 (134)	CF_3CHF
			CHF_2CHF_2	CHF_2CF_2
		5	CHF_2CF_3 (125)	CF_3CF_2
HCFC				
$\text{CH}_{4-m-n}\text{Cl}_m\text{F}_n$ ($1 \leq m \leq 2$) ($1 \leq n \leq 2$) ($2 \leq m+n \leq 3$)		1	CH_2ClF	CHClF
		2	CHCl_2F	CCl_2F
		1	CHClF_2 (22)	CFIF_2
$\text{C}_2\text{H}_{6-m-n}\text{Cl}_m\text{F}_n$ ($1 \leq m \leq 4$) ($1 \leq n \leq 4$) ($2 \leq m+n \leq 5$)		1	$\text{CH}_2\text{ClCH}_2\text{F}$	$\text{CH}_2\text{ClCHF}; \text{CH}_2\text{FCHCl}$
			CH_3CHClF	$\text{CH}_3\text{CClF}; \text{CHClFCH}_2$
		1	$\text{CHClFCH}_2\text{F}$	$\text{CHClFCHF}; \text{CH}_2\text{FCClF}$
			CH_2FCHClF	$\text{CH}_2\text{FCClF}; \text{CHClFCHF}$
			$\text{CH}_2\text{ClCHF}_2$	$\text{CH}_2\text{ClCF}_2; \text{CHF}_2\text{CHCl}$
			CH_3CClF_2	CClF_2CH_2
		1	$\text{CClF}_2\text{CH}_2\text{F}$	CClF_2CHF
			CHF_2CHClF	$\text{CHF}_2\text{CClF}; \text{CHClFCF}_2$
			$\text{CH}_2\text{FCClF}_2$	CClF_2CHF
			CH_2ClCF_3	CF_3CHCl
		1	CF_3CHClF (124)	CF_3CClF
			CCF_2CHF_2	CClF_2CF_2
		2	$\text{CH}_3\text{CCl}_2\text{F}$ (141b)	CCl_2FCH_2
			$\text{CH}_2\text{ClCHClF}$	$\text{CH}_2\text{ClCClF}; \text{CHClFCHCl}$
		2	CHClFCHClF	CHClFCClF
			$\text{CH}_2\text{FCCl}_2\text{F}$	CCl_2FCHF
			$\text{CH}_2\text{ClCClF}_2$	CClF_2CHCl
		2	$\text{CClF}_2\text{CHClF}$	CClF_2CClF
			$\text{CHF}_2\text{CCl}_2\text{F}$	CCl_2FCF_2
			CHCl_2CF_3 (123)	CF_3CCl_2
		3	$\text{CCl}_3\text{CH}_2\text{F}$	CCl_3CHF
			$\text{CHCl}_2\text{CHClF}$	$\text{CHCl}_2\text{CClF}; \text{CHClFCClF}$
			$\text{CH}_2\text{ClCCl}_2\text{F}$	CCl_2FCHCl
		3	$\text{CCl}_2\text{FCHClF}$	CCl_2FCClF
			CCl_3CHF_2	CCl_3CF_2
			$\text{CHCl}_2\text{CClF}_2$	$\text{CClF}_2\text{CCl}_2$
		4	$\text{CHCl}_2\text{CCl}_2\text{F}$	$\text{CCl}_2\text{FCCl}_2$
			CCl_3CHClF	CCl_3CClF

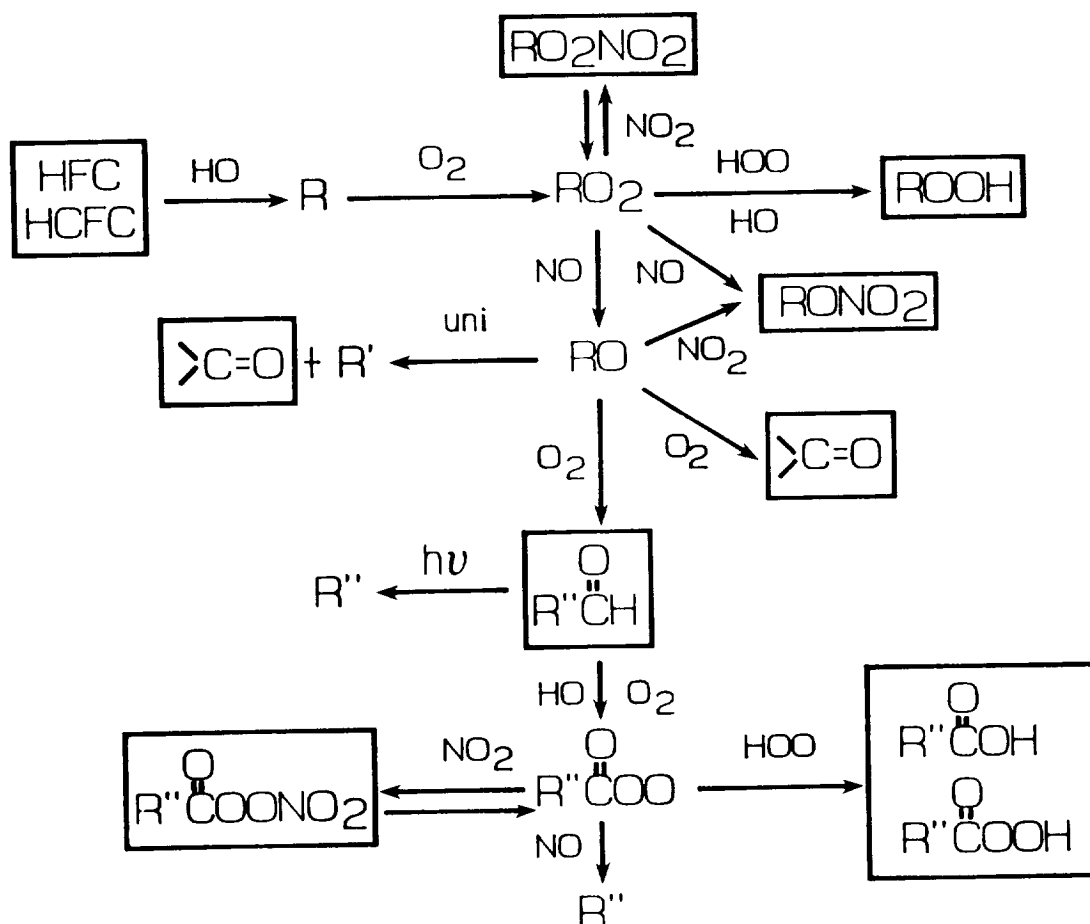
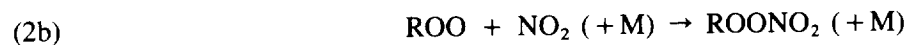


Figure 1: Schematic illustration showing the atmospheric degradation of alternative Fluorocarbons

are enclosed in boxes to differentiate them from the free radical intermediates. Note that under tropospheric conditions the initial haloalkyl (R) radicals exclusively add to O_2 to form the corresponding peroxy RO_2 radicals, (reaction 1).



The most likely reaction partners for these RO_2 radicals in the troposphere are NO , NO_2 or HOO radicals, (reactions 2a-2c) (See, for example, Logan et al., 1981).



In reaction 2a, the ROO radicals are converted by NO into the corresponding haloalkoxy RO radicals, while reactions 2b and 2c yield molecular products haloalkylperoxy nitrate $ROONO_2$ and hydroperoxide

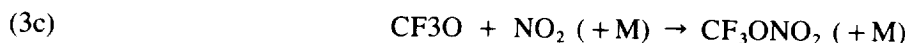
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ROOH, respectively (Niki et al., 1979, 1980b; Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). Although the ROONO₂ products are thermally unstable and readily redissociate back to ROO radicals and NO₂ at temperatures near 300 K, they become sufficiently stable to be the major intermediate products at the colder temperatures encountered in the upper troposphere Simonaitis and Heicklen, 1979. To illustrate, adopting the temperature tabulations in the US standard atmosphere: 288 K (z = 0 km), 249 K (z = 6 km), and 235 K (z = 8 km), the thermal lifetime of CCl₃OONO₂ will be 10 s, 70 min, and 16 hr, respectively Simonaitis and Heicklen, 1979. Also, the haloalkyl hydroperoxides ROOH are the intermediate products which probably react with HO to regenerate ROO radicals, analogous to the HO-reaction of the CH₃OOH produced in the atmospheric oxidation of CH₄ (NASA Report, 1987).

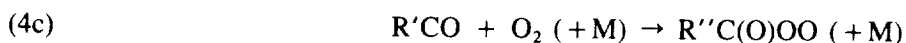
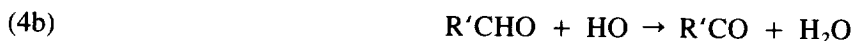
The subsequent fate of the RO radicals appears to vary greatly depending upon the type of the R group, as discussed in detail later. In general, RO radicals are known to lead to the formation of carbonyl compounds, e.g. CF₂O, CClFO, CF₃CFO, CF₃CClO, etc. via unimolecular dissociation, (reaction 3a), and H-atom abstraction by O₂ for those R groups containing hydrogen attached to the oxygenated carbon, (reaction 3b) (Sanhueza, Hisatsune and Heicklen, 1976).



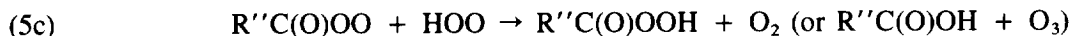
where R' can be either a Cl-atom or a haloalkyl group attached to the oxygenated carbon in the parent R radicals. The R' radicals, in turn, undergo a series of degradation steps similar to those for the R radicals. However, for CF₃O radicals, neither the unimolecular dissociation nor the O₂-reaction are thermochemically feasible, and bimolecular reactions with other reactive atmospheric species such as NO₂, O₂, or HOO are likely to be operative, (reactions 3c - 3e).



Among the carbonyl products, those containing aldehydic hydrogen [-CHO] group probably undergo both photodissociation, (reaction 4a), and bimolecular reaction with HO-radicals to yield peroxy carbonyl radicals, (reactions 4b - 4c).



where R'' represents a haloalkyl group. The R''C(O)OO radicals then react with NO, NO₂ and HOO to form R'' radicals, peroxy nitrates R''C(O)OONO₂, and acids R''C(O)OOH, R''C(O)OH, (reactions 5a - 5c), in a manner analogous to CH₃C(O)OO (NASA Report, 1987; CODATA, 1984).



The peroxy nitrates $R''C(O)OONO_2$ are thermally unstable, but can persist in colder regions of the troposphere because of the strong temperature dependence of reaction 5b, analogous to the behavior of $CH_3C(O)OONO_2$ (PAN) (NASA Report, 1987; CODATA, 1982, 1984), i.e. 3 days at 288 K (0 km); 1 month at 262 K (4 km); 1 yr at 249 K (6 km); 15 yrs at 235 K (8 km). However, the long lifetime probably will not be realized because of the possibility of photodissociation. Notably, while there is no evidence for the existence of the H-substituted carbonylperoxy nitrate $HC(O)OONO_2$, presumably due to thermal instability of its precursor radicals $HC(O)OO$, the corresponding fluorine- and chlorine-substituted peroxy nitrates, $FC(O)OONO_2$ and $ClC(O)OONO_2$ produced via reaction 5b, have been observed in the laboratory, and their thermal dissociation lifetimes appear to be comparable to that of PAN (Edney, Spence and Hanst, 1979).

Summarized in Table 2 are the fluorine- and/or chlorine-containing free radicals and molecular products to be expected in the atmospheric degradation of those HFCs and HCFCs that are of particular interest to the AFEAS assessment, i.e. HFCs-134a, 152a, 125 and HCFCs-22, 123, 124, 141b and 142b. The molecular products include carbonyls, acids, hydroxides and nitrates formed via the reactions illustrated in Figure 1. These products are listed for each alternative fluorocarbon in the consecutive order of occurrence during the course of their degradation. Listed in the 3rd column to the left of the products appearing in each row are their free radical precursors. The H-containing carbonyl products indicated by asterisks are the precursors for those radicals indicated also by asterisks. It can be noted from Table 2 that some free radical precursors and molecular products, particularly fluorinated carbonyls such as $CHFO$, CF_2O and $CClFO$, are common to degradation of many of the HFCs and HCFCs. The expected carbonyl products from all the C1- and C₂-HFCs and HCFCs are listed in Table 3.

3. GAS-PHASE CHEMICAL LIFETIMES IN THE TROPOSPHERE

As already indicated in the preceding section, the atmospheric reactivity of various fluorine- and/or chlorine-containing molecular products can be assessed in terms of three different types of gas-phase chemical reaction, i.e. thermal decomposition, photolysis, and bimolecular reaction with atmospheric species, particularly HO radicals.

Thermal decomposition is important for the peroxy nitrates, $ROONO_2$ and $RC(O)OONO_2$, listed in Table 2. In colder regions of the troposphere, the acylperoxy nitrates $RC(O)OONO_2$ have thermal lifetimes longer than one year and can be considered "stable," while haloalkylperoxy nitrates $ROONO_2$ are short-lived (<1 day) intermediate products. Notably, these peroxy nitrates are present in the troposphere at concentrations equal to or greater than those determined by the equilibrium with their precursors ROO and NO_2 , and they can persist significantly longer than predicted solely from their dissociation rate constants.

Solar radiation in the troposphere contains photons in the near-UV (≤ 295 nm) region which are energetically capable of dissociating various atmospheric compounds (NASA Report, 1987). However, the

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Table 2: Degradation Products in the Tropospheric Oxidation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	HCCl ₂ CF ₃	CF ₃ CCl ₂ OO CF ₃ CCl ₂ O CF ₃ OO CF ₃ O	CF ₃ CClO		CF ₃ CCl ₂ OOH CF ₃ OOH CF ₃ OH	CF ₃ CCl ₂ OONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂
HCFC 141B	CCl ₂ FCH ₃	CCl ₂ FCH ₂ OO CCl ₂ FCH ₂ O CCl ₂ FOO CCl ₂ FO *CCl ₂ FC(O)OO	*CCl ₂ FCHO CClFO	CCl ₂ FC(O)OOH CCl ₂ FC(O)OH	CCl ₂ FCH ₂ OOH CCl ₂ FOOH	CCl ₂ FCH ₂ OONO ₂ CCl ₂ FOONO ₂ CCl ₂ FC(O)OONO ₂
HCFC 142b	CClF ₂ CH ₃	CClF ₂ CH ₂ OO CClF ₂ CH ₂ O CClF ₂ OO CClF ₂ O *CClF ₂ C(O)OO	*CClF ₂ CHO CF ₂ O	CClF ₂ (O)OOH CClF ₂ C(O)OH	CClF ₂ CH ₂ OOH CClF ₂ OOH	CClF ₂ CH ₂ OONO ₂ CClF ₂ OONO ₂ CClF ₂ C(O)OONO ₂
HCFC 22	CHClF ₂	CClF ₂ OO CClF ₂ O	CF ₂ O		CClF ₂ OOH	CClF ₂ OONO ₂
HCFC 124	CHClFCF ₃	CF ₃ CClFOO CF ₃ CClFO CF ₃ OO CF ₃ O	CF ₃ CFO		CF ₃ CClFOOH CF ₃ OOH CF ₃ OH	CF ₃ CClFOONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂
HCF 134a	CH ₂ FCF ₃	CF ₃ CHFOO CF ₃ CHFO CF ₃ OO CF ₃ O *CFO	*CHFO CF ₃ CHFO		CF ₃ CHFOOH CF ₃ OOH CF ₃ OH CF(O)OOH	CF ₃ CHFOONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂ CF(O)OONO ₂
HFC 52a	CHF ₂ CH ₃	CH ₃ CF ₂ Oo CH ₃ CF ₂ O CHF ₂ CH ₂ OO CHF ₂ CH ₂ O CHF ₂ OO CHF ₂ O *CHF ₂ C(O)OO *CFO	CF ₂ O *CHF ₂ CHO *CHFO	CHF ₂ C(O)OOH CHF ₂ C(O)OH CF(O)OOH	CH ₃ CF ₂ OOH CHF ₂ CH ₂ OOH CHF ₂ OOH	CH ₃ CF ₂ OONO ₂ CHF ₂ CH ₂ OONO ₂ CHF ₂ OONO ₂ CHF ₂ C(O)OONO ₂ CF(O)OONO ₂
HCF 125	CHF ₂ CF ₃	CF ₃ CF ₂ OO CF ₃ CF ₂ O CF ₃ OO CF ₃ O	CF ₂ O CF ₃ CFO		CF ₃ CF ₂ OOH CF ₃ OOH CF ₃ OH	CF ₃ CF ₂ OONO ₂ CF ₃ OONO ₂ CF ₃ ONO ₂

Table 3: List of Alternative Fluorocarbons and Carbonyl Radicals

Compound	m	n	Formula	Carbonyl Radical
HFC				
CH _{4-n} F _n (1 ≤ n ≤ 3)		1	CH ₃ F	CHFO
		2	CH ₂ F ₂	CF ₂ O
		3	CHF ₃	
C ₂ H _{6-n} F _n (1 ≤ n ≤ 5)		1	CH ₃ CH ₂ F	CHFO, CH ₃ CFO, CH ₂ FCHO
		2	CH ₃ CHF ₂ (152a)	CHFO, CF ₂ O, CHF ₂ CHO
			CH ₂ FCH ₂ F	CHFO, CH ₂ FCFO
		3	CH ₃ CF ₃	CF ₃ CHO
			CH ₂ FCHF ₂	CHFO, CF ₂ O, CHF ₂ CFO
	4	CH ₂ FCF ₃	CHFO, CF ₃ CFO	
		CHF ₂ CHF ₂	CF ₂ O	
	5	CHF ₂ CF ₃	CF ₂ O	
HCFC				
CH _{4-m-n} Cl _m F _n (1 ≤ m ≤ 2) (1 ≤ n ≤ 2) (2 ≤ m + n ≤ 3)	1	1	CH ₂ ClF	CHFO
	2	1	CHCl ₂ F	CClFO
	1	2	CHClF ₂ (22)	CF ₂ O
C ₂ H _{6-m-n} Cl _m F _n (1 ≤ m ≤ 4) (1 ≤ n ≤ 4) (2 ≤ m + n ≤ 5)	1	1	CH ₂ ClCH ₂ F	CHFO, CHClO, CH ₂ FCHOH, CH ₂ ClCFO
			CH ₃ CHClF	CClFO, CH ₃ CFO, CHClFCHO
	1	2	CHClFCH ₂ F	CHFO, CClFO, CHClFCFO, CH ₂ FCFO
			CH ₂ FCHClF	CHFO, CHClFCFO, CH ₂ FCFO, CH ₂ FCFO
			CH ₂ ClCHF ₂	CHClO, CF ₂ O, CHF ₂ CHO
			CH ₃ CClF ₂	CF ₂ O, CClF ₂ CHO
	1	3	CClF ₂ CH ₂ F	CHFO, CF ₂ O, CClF ₂ CFO
			CHF ₂ CHClF	CHFO, CF ₂ O, CClFO, CHF ₂ CFO
			CH ₂ FCClF ₂	CHFO, CF ₂ O, CClF ₂ CFO
			CH ₂ ClCF ₃	CHClO, CF ₃ CHO
	1	4	CF ₃ CHClF	CF ₃ CFO
			CCF ₂ CHF ₂	CF ₂ O
	2	1	CH ₃ CCl ₂ F	CClFO, CCl ₂ FCHO
			CH ₂ ClCHClF	CHFO, CClFO, CH ₂ ClCFO, CHClFCHO
	2	2	CHClFCHClF	CClFO, CHClFCFO
			CH ₂ FCCl ₂ F	CHFO, CClFO, CCl ₂ FCFO
			CH ₂ ClCClF ₂	CHClO, CClF ₂ CHO
	2	3	CClF ₂ CHClF	CF ₂ O, CClFO, CClF ₂ CFO
			CHF ₂ CCl ₂ F	CF ₂ O, CClFO
			CHCl ₂ CF ₃	CF ₂ CClO, CCl ₂ O
	3	1	CCl ₃ CH ₂ F	CHFO, CCl ₂ O, CCl ₃ CFO
			CHCl ₂ CHClF	CHFO, CHClO, CHCl ₂ CFO, CHClFCClO
			CH ₂ ClCCl ₂ F	CHClO, CClFO, CCl ₂ FCHO
	3	2	CCl ₂ FCHClF	CClFO, CCl ₂ CFO
			CCl ₃ CHF ₂	CF ₂ O, CCl ₂ O
			CHCl ₂ CClF ₂	CF ₂ O, CCl ₂ O, CClF ₂ CClO
	4	1	CHCl ₂ CCl ₂ F	CClFO, CCl ₂ O, CCl ₂ FCClO
			CCl ₃ CHClF	CClFO, CCl ₂ O, CCl ₃ CFO

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data for UV absorption cross sections and quantum yields required for determining photodissociative lifetimes are not available for the majority of the fluorine-containing products listed in Table 2. Carbonyl compounds such as CF_2O , CClFO and CCl_2O are known to lack absorptions in the near-UV region and thus, are photochemically inactive in the troposphere (NASA Report, 1987). On the other hand, those RCHO compounds with R = haloalkyl group are known to absorb UV at wavelengths longer than 300 nm (Calvert and Pitts; 1967), but their quantum yields for the formation of $\text{R} + \text{HCO}$ and $\text{RH} + \text{CO}$ under atmospheric conditions have not been determined. In the absence of the necessary information, all the carbonyls listed in Table 2 should be regarded as being potentially photochemically stable. The haloalkyl acids also appear to be photochemically inactive, since the first UV absorption bands of the organic acids generally lie below 250 nm (Calvert and Pitts; 1967). The onset of absorption for the ROOH compounds listed in Table 2 is likely to occur at wavelengths longer than 295 nm, by analogy to H_2O_2 and CH_3OOH (NASA Report; 1987). The latter peroxides can decay photochemically in the troposphere, splitting the O-O bond, at noon photolysis rates of approximately 1 day⁻¹ and thus, short photochemical lifetimes are also expected for the haloalkyl hydroperoxides. There appears to be no information on the photochemical properties of the haloalkyl-substituted RC(O)OONO_2 compounds, although they are not expected to be strong absorbers in the near-UV region. The UV spectrum of even the most common compound of this type, i.e. PAN ($\text{R} = \text{CH}_3$), is not sufficiently well-characterized to exclude significant photolysis in the middle and upper troposphere.

Reaction with HO radicals can be responsible, at least in part, for the subsequent degradation of various hydrogen-containing products listed in Tables 2 and 3, depending on their HO-radical reactivity. Among the aldehydic products RCHO , all those containing R = haloalkyl group probably react rapidly with HO radicals. For instance, a room temperature rate constant of $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the $\text{HO} + \text{CCl}_3\text{CHO}$ reaction (Logan et al.; 1981; Crutzen, 1982; WMO Report; 1985) combined with the global average HO concentration of $5 \times 10^5 \text{ molecule cm}^{-3}$ (Crutzen, 1982) gives a lifetime of about 12 days. Although not firmly established experimentally, halogen-substitution for the aldehydic products RCHO ($\text{R} = \text{F}$ or Cl atom) should greatly reduce their reactivity towards HO radicals [cf. Appendix], and their corresponding atmospheric lifetimes are likely to be as long as several months. For the carbonyls and other products containing hydrogen in the haloalkyl groups only, rate constants for H-abstraction are expected to be comparable to those for the corresponding haloalkanes, leading to lifetimes typically longer than one year. The HO-reactivity of the haloalkyl-substituted acidic products RC(O)OH is expected to be similar to that of HC(O)OH and $\text{CH}_3\text{C(O)OH}$ (Atkinson, 1985), and their estimated atmospheric lifetimes are about a month or longer. On the other hand, the HO-group in a peroxy acid RC(O)OOH is expected to be much less reactive towards HO radicals due to internal hydrogen-bonding to the $\text{C}=\text{O}$ group. It remains to be determined whether H abstraction from the HO groups in haloalkyl-substituted alcohols and hydroperoxides will occur at rates comparable to those of their alkyl counterparts. For comparison, room temperature rate constants for the H abstraction from the CH_3 groups of CH_3OH and CH_3OOH are approximately 1×10^{-13} and $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, i.e. lifetimes of 8 months and 5 days, respectively. Among the RONO_2 and RC(O)OONO_2 compounds listed in Table 2, only $\text{CHF}_2\text{C(O)OONO}_2$ formed from HFC-152a contains hydrogen. This compound is expected to react with HO radicals more slowly than $\text{CH}_3\text{C(O)OONO}_2$ [PAN]. The rate constant for PAN is $1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, corresponding to a lifetime of approximately 6 months.

The preceding semi-quantitative discussion concerning atmospheric reactivity of various degradation

products suggests that F- and/or Cl-substituted alkyl compounds generally have substantially longer lifetimes than their alkyl counterparts. There appear to be no known gas-phase reactions for the removal of fully halogenated carbonyls and nitrates.

4. SUMMARY

Tropospheric gas-phase degradation mechanisms and products of alternative fluorocarbons have been assessed based on available laboratory data. The fluorine- and/or chlorine-substituted haloalkyl radicals formed from HFCs and HCFCs after H atom abstraction by HO radicals appear to undergo atmospheric transformations largely analogous to those of the corresponding alkyl radicals. The molecular products include a large variety of fluorine- and/or chlorine-containing carbonyls, acids, peroxy acids, alcohols, hydrogen peroxides, nitrates and peroxy nitrates. Probable atmospheric lifetimes of these compounds have also been estimated. For some carbonyl and nitrate products there seem to be no significant gas-phase removal mechanisms.

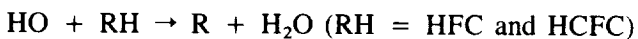
5. ACKNOWLEDGEMENTS

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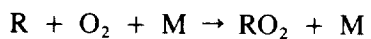
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APPENDIX: LITERATURE REVIEW OF THE RELEVANT GAS-PHASE REACTIONS

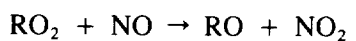
This review focuses primarily on aspects of the literature information which are not included in the kinetic data evaluation reports published by the NASA and CODATA panels (NASA Report, 1987; CODATA, 1982, 1984). Some of the studies cited are highly qualitative but provide important information for the present assessment. It is not intended as recommendation for modeling purposes.



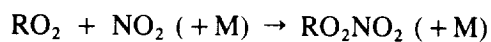
The rate constants for these reactions appear to be well established (NASA Report, 1987). For those C₂-fluorocarbons containing H atoms attached to both the A- and B-carbon atoms, H-atom abstraction from either carbon can occur, but the product distribution is largely unknown. The only available experimental value is that for CH₃CH₂F; 85% ± 4% for abstraction from the A-carbon (HO + CH₃CH₂F → H₂O + CH₃CHF) (Singleton, Paraskevopoulos and Irwin, 1980). Empirical correlations between the rate constant and C-H bond energy do not work well for predicting product distributions (Atkinson, 1985). Recommendations based on transition-state-theory calculations and the above-mentioned single experimental measurement at room temperature are also available for extrapolation to other temperatures and to other fluorocarbons (Cohen and Westberg, 1988). In the present assessment, all possible primary radicals and their reaction products are considered, as indicated in Tables 1-3.



Limiting high pressure rate constants of > 10⁻¹² cm³ molecule⁻¹ s⁻¹ have been reported for R = CF₃ (Ryan and Plumb, 1982), CCl₂F (Caralp and Lesclaux, 1983; Caralp, Dognon and Lesclaux, 1984), and CCl₃ (Cooper et al., 1980; Ryan and Plumb, 1984). These rate constants are comparable to those for R = CH₃ (NASA Report, 1987; CODATA, 1982, 1984). Similar values are expected for all the R species listed in Table 1. Under tropospheric conditions, these addition reactions seem likely to be the exclusive reaction path for R radicals.



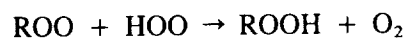
The rate constants for R = CF₃, CF₂Cl, CFCl₂, and CCl₃ are recommended by the NASA panel report are based on existing experimental data (Caralp, Dognon and Lesclaux, 1984; Ryan and Plumb, 1984; Lesclaux and Caralp, 1984; Dognon, Caralp and Lesclaux, 1985; Plumb and Ryan, 1982). The room-temperature rate constants of 1.5-1.7 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ are comparable to the NASA-recommended value of 7.6 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ for R = CH₃ (NASA Report, 1987). In these reactions NO₂ has been shown to be the major nitrogen-containing product (Ryan and Plumb, 1984). Some of the RO₂ radicals may yield RONO₂ as well as RO + NO₂ upon reaction with NO under atmospheric conditions, analogous to the alkyl radicals (≥ C₄) (Carter and Atkinson, 1985). Thus, in the present assessment, both possibilities are indicated in Figure 1 and Tables 2-3.



These reactions appear to be highly competitive with reaction 2a under tropospheric conditions. For

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$R = CCl_3$, the ratio of rate constants $k_{2b}/k_{2a} = 0.68$ has been reported at 1 atmosphere, independent of temperature (Simonaitis and Heicklen, 1979; Lesclaux and Caralp, 1984). For $R = CFCI_2$, a high pressure limit of $k_{2b} = 6.0 (\pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been determined based on extrapolation from the data obtained at the diluent O_2 pressures of 1-12 torr. The unimolecular rate constants for the thermal dissociation of the haloalkyl and alkylperoxy nitrates are probably all similar, e.g. $k_{-2b} = 10^{15.56 \pm 1.00} \exp[(-11\,000 + 600/T)] \text{ s}^{-1}$ for $R = CCl_3$ (Simonaitis and Heicklen, 1979).



By analogy to $\text{ROO} = \text{CH}_3\text{OO}$ (NASA Report, 1987; CODATA, 1982, 1984), the HOO -reactions of haloalkyl-substituted ROO radicals are probably competitive with reactions 2a and 2b. No kinetic data are available for these reactions. For $R = \text{CH}_2\text{Cl}$ and CHCl_2 , there is IR spectroscopic evidence for the formation of ROOH products (Niki et al., 1980b). However, the possibility of an alternative mechanism to form $>\text{C}=\text{O} + \text{H}_2\text{O} + \text{O}_2$ via formation of an adduct $[\text{ROOOH}]$ complex formation has not been entirely ruled out. The products, haloalkyl hydroperoxides, are intermediate products which are likely to react further with HO radicals to regenerate ROO radicals, in analogy to the reaction of CH_3OOH (NASA Report, 1987; CODATA, 1982, 1984).

Reactions Involving RO Radicals

The atmospheric reactions of the haloalkoxy RO radicals are less well established. Product studies have been carried out at room temperature and atmospheric pressure of air for the following RO radicals; $\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{CHClO} + \text{HO}_2$ (Simonaitis and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $\text{CHCl}_2\text{O} \rightarrow \text{CHClO} + \text{Cl}$ (Simonaitis and Heicklen, 1979; Sanhueza and Heicklen, 1975a); $\text{CF}_3\text{-xCl}_x\text{O} \rightarrow \text{CF}_3\text{-xCl}_{x-1}\text{O} + \text{Cl}$ ($1 \leq x \leq 3$) (Jayanty, Simonaitis and Heicklen, 1975; Gillespie, Garraway and Donovan, 1977; Suong and Carr, 1982); $\text{CCl}_3\text{CCl}_2\text{O} \rightarrow (\text{CCl}_3\text{CClO} + \text{Cl})/(\text{CCl}_3 + \text{CCl}_2\text{O}) = 6.0$ (Mathias et al., 1974; Hybrechts, Olbregts and Thomas, 1967); $\text{CHCl}_2\text{CCl}_2\text{O} \rightarrow (\text{CH}_2\text{ClCClO} + \text{Cl})/(\text{CHCl}_2 + \text{CCl}_2\text{O}) > 6.0$ (Hybrechts and Meyers, 1966; Bertrand et al., 1968); $\text{CH}_2\text{ClCCl}_2\text{O} \rightarrow (\text{CH}_2\text{ClCClO} + \text{Cl})/(\text{CH}_2\text{Cl} + \text{CCl}_2\text{O}) < 50$ (Sanhueza and Heicklen, 1975b); $\text{CHCl}_2\text{CHClO} \rightarrow (\text{CHCl}_2\text{CHO} + \text{Cl})/(\text{CHCl}_2 + \text{CHClO}) < 50$ (Sanhueza and Heicklen, 1975c); $\text{CH}_2\text{ClHCHClO} \rightarrow (\text{CH}_2\text{ClHCHO} + \text{Cl})/(\text{CH}_2\text{ClH} + \text{CHClO}) > 10$ (Sanhueza and Heicklen, 1975c); $\text{CClF}_2\text{CCl}_2\text{O} \rightarrow (\text{CClF}_2\text{CClO} + \text{Cl})/(\text{CClF}_2 + \text{CCl}_2\text{O}) > 10$ (Simonaitis and Heicklen, 1979); $\text{CF}_2\text{ClCF}_2\text{O} \rightarrow \text{CF}_2\text{Cl} + \text{CF}_2\text{O}$ (Simonaitis and Heicklen, 1979). Some general trend in the degradation mechanisms can be inferred from these studies (Simonaitis and Heicklen, 1979), i.e.

- * The strong C-F bonding is not broken during the course of the degradation.
- * H atom abstraction by O_2 is the dominant reaction for those R radicals containing two H atoms attached to the oxygenated carbon atom, and also for one carbon RO containing only H and F atoms.
- * For $R = R''\text{CHFO}$ where R'' is a haloalkyl group, the predominant reaction is unimolecular decomposition.
- * For those R groups containing one H and one or more Cl attached to the oxygenated carbon atom, the ROO radicals may predominantly undergo unimolecular dissociation by either breaking the C-Cl

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and/or C-C bond depending upon the exothermicity of these two channels. In this assessment, both possibilities are included for all these ROO radicals.

For $R = CF_3O$, the O_2 -reaction $CF_3O + O_2 \rightarrow CF_2O + FO_2$ and the unimolecular dissociation $CF_3O \rightarrow CF_2O + F$ are endothermic by 29 and 22 kcal/mole (Herron, 1989), respectively, so other bimolecular reactions such as those with NO_2 , HOO or O_3 are likely to occur, as indicated in the text.

Reactions Involving RCHO ($R = F, Cl$ or haloalkyl group)

Although no data seem to be available, both photodissociation and HO-reaction may play a role in the atmospheric removal of the RCHO compounds. Note that if UV absorption spectra of HCFO and HCClO resemble those of CF_2O and CCl_2O rather than that of HCHO (NASA Report, 1987), these RCHO compounds cannot photodissociate in the troposphere. Also, F- or Cl-substitution should greatly reduce their reactivity towards HO radicals analogous to the Cl-atom reaction of HCHO and HCClO (Sanhueza and Heicklen, 1975a; Niki et al., 1980a). On the other hand, those RCHO compounds with $R =$ haloalkyl group are known to absorb UV at wavelength longer than 300 nm (Calvert and Pitts, 1967), but the quantum yields for the formation of $R + HCO$ and $RH + CO$ under atmospheric conditions have not been determined. The HO-reactions of these RCHO compounds and their subsequent reactions are probably analogous to that of CH_3CHO (NASA Report, 1987; CODATA, 1982,1984), but their HO-rate constants are probably much smaller than $1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CH_3CHO at 298 K. For instance, a room temperature value of $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been determined for CCl_3CHO (Nelson, Treacy and Sidebottom, 1984). This value may be used as an upper limit for estimating the atmospheric lifetimes of the RCHO compounds in this assessment.

The F, Cl or haloalkyl-substituted $RC(O)OO$ radicals are expected to undergo reactions with NO , NO_2 and HOO , (reactions 5a - 5c), analogous to $CH_3C(O)OO$ radicals (NASA Report, 1987; CODATA, 1982,1984). Except for the IR spectroscopic observation of $FC(O)OONO_2$ and $ClC(O)OONO_2$ and the thermal dissociation of $ClC(O)OONO_2$ (Edney, Spence and Hanst, 1979), no quantitative data are available on the kinetics of these reactions. The rate constants for the reaction $ClC(O)OONO_2 \rightarrow ClC(O)OO + NO_2$ have been determined over the temperature range of 293.7 to 300.3 K in air at 1 atm pressure to be $10^{16.8 \pm 1.5} \exp(-27.7 \pm 2.3 \text{ kcal/mol}) \text{ s}^{-1}$ (Edney, Spence and Hanst, 1979). This expression is comparable to the rate expression of $1.12 \times 10^{16} \exp(-13330/T)$ for $R = CH_3$ (CODATA, 1982,1984).